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ENVIRONMENTAL FAILURE OF  
ADHESIVE BONDING IN COMPOSITES

FIRST ANNUAL REPORT

by

E.H. Andrews, Ho Ping Sheng, H.A. Majid  
and C. Vlachos

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The adaptation of the Andrews-Stevenson (A-S) adhesion test, previously used for epoxy to metal adhesive systems, for epoxy to glass bonds has been achieved for epoxy resins having relatively low T<sub>g</sub>'s (e.g. Epibond 820).

*T<sub>g</sub> = 71°C*

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$T_g = 71^\circ\text{C}$ ). Partial success has been achieved for high  $T_g$  resins (e.g. SP250). This adaptation has required considerable sophistication of test-piece geometry to prevent thermal contraction stresses shattering the glass substrates during specimen preparation.

The effect of water immersion at  $80^\circ\text{C}$  for various periods of time has been studied for the system Epikote 828 pyrex glass in the absence of coupling agents. The fracture mode becomes increasingly cohesive as immersion time increases and the peak in the curve of fracture energy versus crack speed falls progressively. Using Andrews' generalized theory, the adhesive fracture energy  $\theta$  can be separated into its interfacial energy and dissipative components. The interfacial energy  $\theta_0$  is found to decrease exponentially with time, from its cohesive value of approximately  $2.6 \text{ J/m}^2$  to some  $0.13 \text{ J/m}^2$  after 100 h immersion at  $80^\circ\text{C}$ . The nature of the decrease is indicative of a first order chemical hydrolysis reaction at the interface. The value of  $\theta_0$  after 100 h is much less than the residual value ( $\sim 0.7 \text{ J/m}^2$ ) for similar treatments when the substrate is titanium metal rather than glass. It suggests that spontaneous separation of resin from glass may eventually occur.

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## ENVIRONMENTAL FAILURE OF ADHESIVE BONDING IN COMPOSITES

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### SUMMARY

This is the first annual report under grant No. DAERO/78/G/118 which commenced on 1st October 1978. The report covers the period from that date up to 31st December 1979.

The adaptation of the Andrews-Stevenson (A-S) adhesion test, previously used for epoxy to metal adhesive systems, for epoxy-to-glass bonds has been achieved for epoxy resins having relatively low  $T_g$ 's (e.g. Epikote 828,  $T_g = 71^\circ\text{C}$ ). Partial success has been achieved for high  $T_g$  resins (e.g. SP250). This adaptation has required considerable sophistication of test-piece geometry to prevent thermal contraction stresses shattering the glass substrates during specimen preparation.

The effect of water immersion at  $80^\circ\text{C}$  for various periods of time has been studied for the system Epikote 828 / pyrex glass in the absence of coupling agents. The fracture mode becomes increasingly cohesive as immersion time increases and the peak in the curve of fracture energy versus crack speed falls progressively. Using Andrews' generalized theory, the adhesive fracture energy  $\Theta$  can be separated into its interfacial energy and dissipative components. The interfacial energy  $\Theta_0$  is found to decrease exponentially with time, from its cohesive value of approximately  $2.6 \text{ J/m}^2$  to some  $0.13 \text{ J/m}^2$  after 100 h immersion at  $80^\circ\text{C}$ . The nature of the decrease is indicative of a first order chemical hydrolysis reaction at the interface. The value of  $\Theta_0$  after 100 h is much less than the residual value ( $\sim 0.7 \text{ J/m}^2$ ) for similar treatments when the substrate is titanium metal rather than glass. It suggests that spontaneous separation of resin from glass may eventually occur.

## 1. INTRODUCTION

Considerable success has been achieved in studying epoxy resin-to-metal bonding by the use of plane-strain testing technique for adhesive bonds due to Andrews and Stevenson [1]. We shall refer to this test as the A-S test. The method involves the inflation by air pressure of an otherwise totally enclosed, penny shaped, crack situated at the interface between a substrate and a block of adhesive. The adhesive fracture energy ( $\Theta$ ) is obtained from the specimen dimensions and the critical pressure for fracture [1]. Because epoxy resins exhibit rate-sensitive fracture behaviour, the velocity of the fracture front has been measured for each test using high-speed photography.

In studies of an epoxy resin (Shell Epikote 828) adhering to untreated titanium metal, it has been possible to determine the dependence of  $\Theta$  upon  $\dot{c}$  (crack velocity) and thence to deduce the atomic interaction energy  $\Theta_0$  at the interface and its variation with time and temperature of immersion in water. A marked effect of water pH value was also found upon  $\Theta_0$  [2]. It was possible to make the following deductions:-

- i) The initial 'dry' value of  $\Theta_0$  was some ten times the value expected from Van der Waals bonding at the interface. This can be interpreted as meaning that some 9% of the interfacial bonds are primary bonds.
- ii) The destruction of the interfacial bonding by water is a first-order chemical hydrolysis reaction whose rate-constants are derived. The rate constant is considerably larger for acid than for alkaline conditions.

iii) The probable chemistry of interfacial degradation is an acid catalysed hydrolysis of ether linkages between the resin and the oxidised Ti surface.

The purpose of the current studies on epoxy-to-glass bonds is to repeat the kind of experiments carried out with metals and derive similar information. In particular we wished to see whether the degradation of interfacial bonds in aqueous environments followed a similar pattern to that established for titanium and to see how coupling agents modify this process. These results are expected to throw light on the bonding in glass reinforced thermoplastics and its deterioration in aqueous environments.

## 2. MATERIALS

The two resins employed are:-

- a) a diglycidyl ether of bisphenol A, of molecular mass  $\sim 370$  (Shell Epikote 828), cured by a hardener consisting of a blend of two cycloaliphatic amines with added benzyl alcohol as an accelerator (Shell Epikure 114). After outgassing at  $60-70^{\circ}\text{C}$  the components were mixed in the stoichiometric ratio of five parts of resin to two parts of hardener. After casting, specimens were left to gel at room temperature for 24h. and postcured at  $130^{\circ}\text{C}$  for 1.5h. This procedure was found to give a maximum glass transition temperature ( $71^{\circ}\text{C}$ ). Final cooling was carried out at  $0.5^{\circ}\text{C}/\text{minute}$ .
- b) A two-component resin manufactured by 3M's Corporation and denoted SP250. The catalyst system is a mixture of an unspecified accelerator and "dicy" ( $(\text{NH}_2)_2\text{C}=\text{N}-\text{C}\equiv\text{N}$ ) in the form of a crystalline powder. The resin was heated to  $80^{\circ}\text{C}$ , mixed thoroughly and transferred to small glass containers for subsequent use. The resin was stored at  $-10^{\circ}\text{C}$ . Mixes were prepared for casting by heating to  $88^{\circ}\text{C}$  and adding 12.83 parts by weight of catalyst to every 100 parts of resin. (This gives 11.37% by weight of catalyst,

containing 7.54% of "dicy" and 3.83% of accelerator). The mix was homogenized using a 'lightning' mixer for 5 to 10 minutes.

The temperature was allowed to drop to 82°C before casting (this is the manufacturers' 'normal use' temperature). Curing is recommended at 127°C for 2h. To control exothermic heat generation and foaming we are currently using the following procedure.

- a) Leave cast specimens at room temperature for 24h.
- b) Heat to 95°C and hold for 2h at 95°C
- c) Heat at 3°C/min. to 127°C and hold for 2h.
- d) Cool at 3°C/min.

The effect of varying the cure cycle on adhesive properties will be studied in due course.

### 3. THE RESIN-GLASS TESTPIECE

Great difficulty has been encountered in constructing resin/glass test specimens similar to those used routinely for resin/metal studies. The reason for this lies in the proneness of the glass to brittle fracture induced either by the 'inflation' pressure during the test or by differential thermal contraction of the resin.

After various test-piece configurations had been tried, the problem of fracture under the inflating pressure during test was finally solved by cementing the glass sheet to a metal base block by means of 'instant glue'.

The problem of fracture due to thermal contraction has proved more intractable. With Epikote 828 resin with a  $T_g$  of 71°C no fracture occurs during specimen preparation, but exposure to water eventually produces a cone fracture in the glass after the de-bonding boundary has penetrated inwards by a critical distance.

The difficulty was eventually overcome in the following manner.

- a) Low  $T_g$  epoxy resin (Epikote 828). The original specimen design (Fig.1)



was modified as shown in Fig.2. The major difference is that the outer circumference of the cast epoxy block is no longer in contact with the glass surface but is carried instead on a steel 'washer' which is itself attached to the glass by a thin layer of the epoxy resin. The differential thermal contraction of the glass and resin gives rise to shear stresses, estimated by photoelastic measurements (see Fig.3) at some  $4.7 \text{ MN/m}^2$ , which reach their maximum value at the outer edges of the epoxy block. With the modified design of specimen these maximum shear stresses are carried by the annular metal washer rather than the glass surface. It has been found essential to grind the surface of the washer flat and stick it down to the glass with resin. Without these precautions specimens fail spontaneously (by the familiar cone-cracking of the glass) during immersion in water.

- b) High  $T_g$  resin (3M's SP 250). Also suitable for low  $T_g$  resins  
 Even the above precautions have failed to yield intact specimens using SP 250 resin. The thermal contraction stresses referred to earlier are of course proportional to  $(T_g - T_a)$  where  $T_g$  is the glass transition temperature and  $T_a$  is the ambient temperature. A high  $T_g$  thus automatically leads to large shear stresses tending to rip the glass substrate apart.

An alternative approach has therefore been adopted for high  $T_g$  resins, and is shown in Fig.4. A thin layer of resin is sandwiched between two glass sheets, with the penny-shaped crack established as usual by the inclusion of a thin PTFE disc. The layer of resin is now, however, no thicker than the disc, itself, so that crack initiation may occur at upper or lower resin interfaces. The formula giving  $\theta$  from the critical pressure will have to be modified for this form of test piece, but we do not anticipate difficulty in doing this

since most of the 'far field' contribution to the energy release rate [1] will come from the upper glass sheet.

Test pieces of this design using SP 250 have now been successfully tested and provide the added bonus that, because the resin layer is thin, transparency is preserved allowing crack propagation rates to be measured photographically as before.

#### 4. ANALYTICAL INFORMATION

This information has been published already [1,2], but is repeated here for the reader's convenience.

The fracture energy for cohesive fracture of the resin is denoted  $2\gamma$ , this being the energy required to create unit area of fresh crack plane consisting of two identical surfaces (hence the factor two).

For the A-S test configuration,

$$2\gamma = \frac{P_c^2 c}{Ef_1(h/c)} \quad (1)$$

where  $P_c$  is the critical pressure,  $c$  is the radius of the artificial penny-shaped crack,  $E$  is the Young's modulus of the resin and  $f_1$  is a complicated function of  $c$  and  $h$  (the height of resin above the crack) given in references [1,2].

When cohesive fracture occurs it has the form of a cone crack propagating upwards into the resin and expelling a truncated conical section of resin.

After joints have been weakened by exposure to water, failure becomes interfacial, the crack propagating wholly or partly along the interface between substrate and adhesive. In this case we calculate the adhesive fracture energy,  $\theta$ , which is analogous to  $2\gamma$ . The formula for  $\theta$  is

$$\theta = \frac{P_c^2 c}{Ef_2(h/c)} \quad (2)$$

i.e. the same formula as for  $2\gamma$  except that  $f_1$  is replaced by a similar

function  $f_2$  which differs in that it takes account of the proximity of the rigid substrate to the fracture front.

According to generalized fracture mechanics theory [3],

$$2\gamma = 2\gamma_0 \Phi(\dot{c}, T) \quad (3)$$

$$\theta = \theta_0 \Phi(\dot{c}, T) \quad (4)$$

where  $2\gamma_0$  and  $\theta_0$  are respectively the cohesive and adhesive interfacial energies [2,4] and  $\Phi$  is the loss function for the resin. By plotting  $\log 2\gamma$  or  $\log \theta$  against  $\dot{c}$  curves are thus obtained which reflect the variation of  $\Phi$  with  $\dot{c}$  due to visco-elastic and plastic energy losses, and which are displaced from one another along the  $\log \theta$  axis by distances equal to  $\log(\theta_{01}/\theta_{02})$  where  $\theta_{01}$ ,  $\theta_{02}$  are the relevant  $\theta_0$  values for any two curves being compared.

Provided, therefore,  $\Phi$  does not vary with time of immersion in water it is possible:-

a) to obtain a master curve from all data at a given temperature by shifting curves along the  $\log \theta$  axis.

b) to obtain a  $\theta_0$  value for each time and condition of immersion.

Relative  $\theta_0$  values are obtained directly from the shifts; absolute values require a knowledge of  $2\gamma_0$  which has been obtained previously for Epikote 828, though not yet for SP 250.

c) In consequence of (b) to determine the manner in which  $\theta_0$ , which is the interfacial atomic interaction energy, varies with time, temperature and environment.

## 5. RESULTS

Figure 5 shows data for Epikote 828 bonded to float glass (cleaned only in water and acetone) and immersed for different periods of time in tap water at 80°C. As the time of immersion increases from zero to 20, 40 and 100h, the curve of  $2\gamma$  or  $\theta$  against  $\dot{c}$  falls progressively as shown. The data were plotted logarithmically and a master curve

constructed as shown in Fig. 6. This master curve is very similar to that obtained for the same epoxy resin bonded to titanium. With the epoxy-titanium system it was observed that the peak in the curve shifted to higher velocities as water was absorbed over the first 60h or so. At longer immersion times the peak remained at about 40 m/s. None of the immersion times used here exceeded 100h, and it is not surprising to find that the peak occupies an intermediate position around 30 m/s with some evidence of a gradual shift with time as observed previously. The loss function  $\phi$  thus appears to behave independently of the nature of the substrate, whether metal or glass, as is of course expected from theory.

Figure 7 shows the behaviour of the atomic interaction parameter (or interfacial energy)  $\theta_o$ . This quantity is obtained from the shifts required to superimpose data on to a master curve, together with a value of the intrinsic cohesive fracture energy  $2\gamma_o$  obtained from calculation and cohesive fracture measurements on the epoxy resin above its  $T_g$  [5].

The data for the immersed specimens show a logarithmic dependence of  $\theta_o$  upon time, indicative of a first order chemical hydrolysis reaction,

$$\frac{d\theta_o}{dt} = -k \theta_o \quad (5)$$

with a rate constant  $k = 3.7 \cdot 10^{-2} \text{ h}^{-1}$  (at  $80^\circ\text{C}$  and neutral pH). This is about six times larger than the comparable rate constant for the same resin bonded to titanium metal, indicating a faster hydrolysis reaction and thus, probably, a different form of interfacial bonding.

The extrapolated value of  $\theta_o$  at zero time of immersion is  $4.37 \text{ Jm}^{-2}$ , significantly larger than the value of  $2.59 \text{ Jm}^{-2}$  for  $2\gamma_o$  in dry resin [5]. This, of course, accounts for the dry specimens breaking cohesively and suggests that the beginnings of adhesive mode failure should be observed after about 15 h immersion at  $80^\circ\text{C}$  which is in line with observation.

Insufficient results have yet been obtained with the SP 250 resin to reproduce them here. Before doing so, in any case, it will be necessary to ascertain what effect, if any, is caused in the loss function  $\Phi$  by the sandwich specimen geometry which has had to be adopted for this material. This will be done using Epikote 828 in sandwich specimens for comparison with the normal cast specimens. Current work is thus directed towards this end as well as to ascertaining the effects of coupling agents on the durability of the Epikote 828/glass system.

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# CAPTIONS TO DIAGRAMS

Fig. 1 Original specimen design for the A-S test. Circular symmetry about A-A; B ptfe disc; D orifice; E base block/substrate; F resin.

Fig. 2 Modified design for epoxy resins on glass, showing steel washer introduced to carry the maximum shear stresses.

Fig. 3 Specimen as in Fig. 2 viewed by transmitted light between crossed polars and showing stress-optical fringes due to shear stresses at interface.

Fig. 4 Sandwich specimen for high  $T_g$  resins, showing; A glass substrate; B glass cover plate; C resin; D ptfe disc; E ptfe spacers.

Fig. 5 Fracture energy versus crack velocity for Epikote 828 bonded to float glass after immersion in water at  $80^{\circ}\text{C}$  for the times indicated.

Fig. 6 Master curve constructed from log-log plots of the data from Fig. 5.

Fig. 7 Variation of  $\log \theta_o$  with time of immersion. Filled point is cohesive ( $2T_o$ ) value.

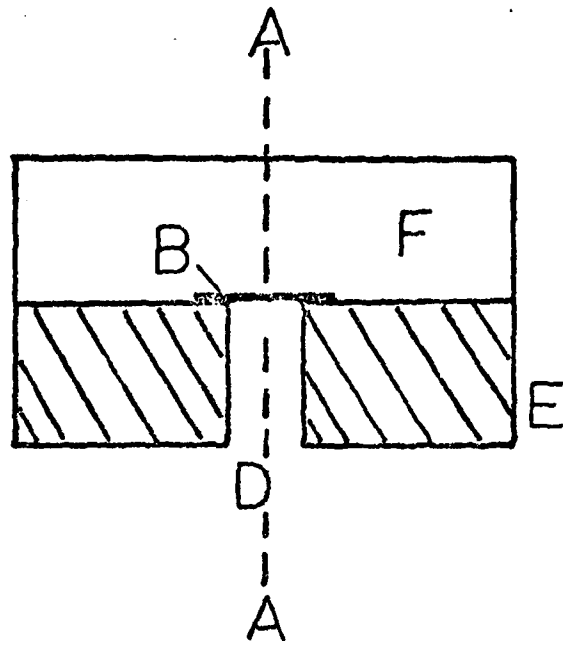


FIG 1

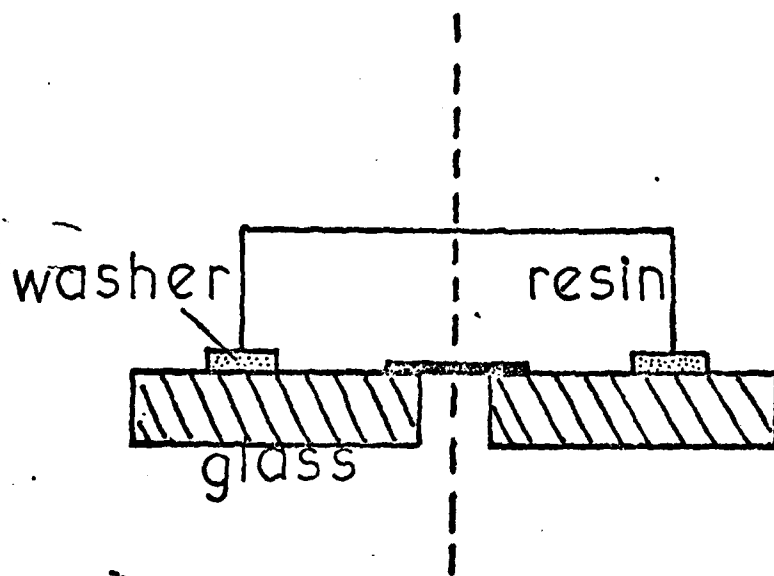


FIG 2



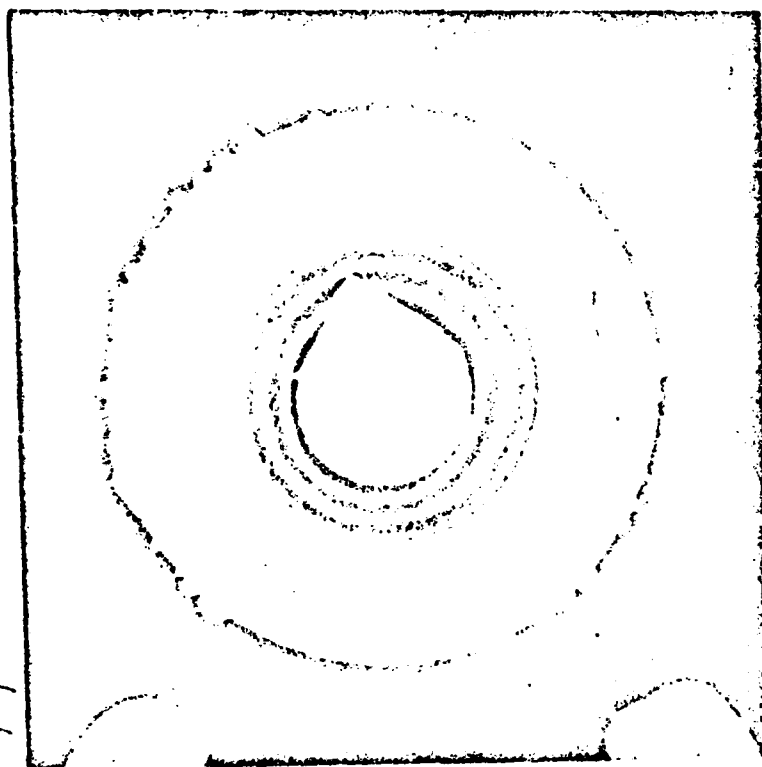


FIG 3

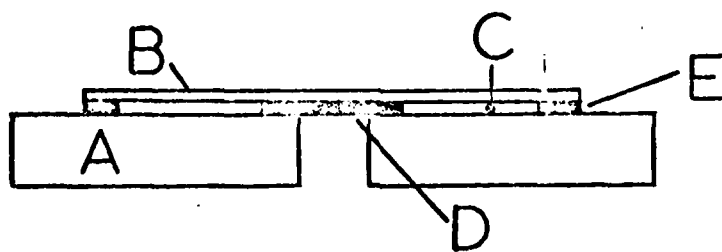


FIG 4

FIG 5

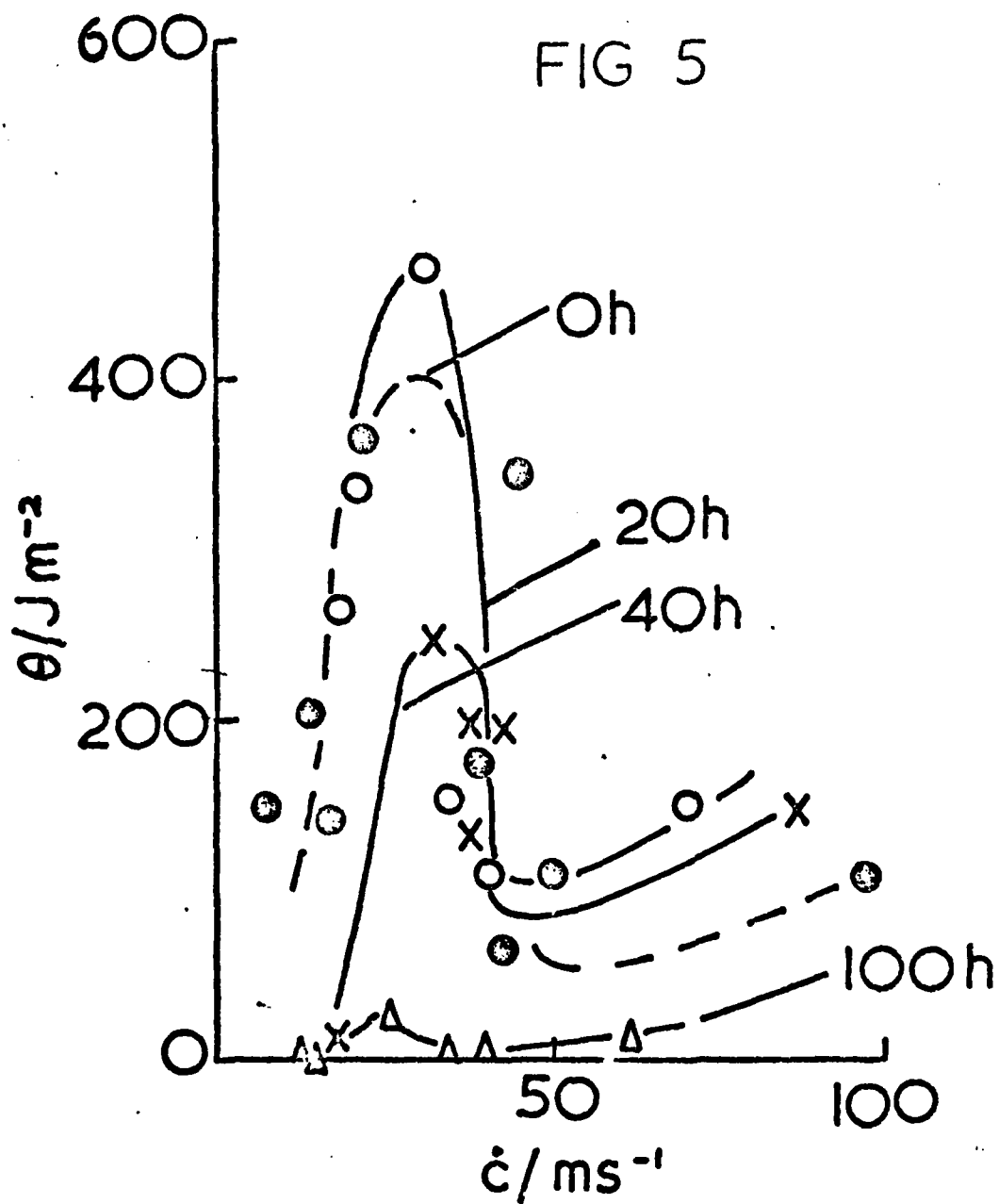


FIG 6

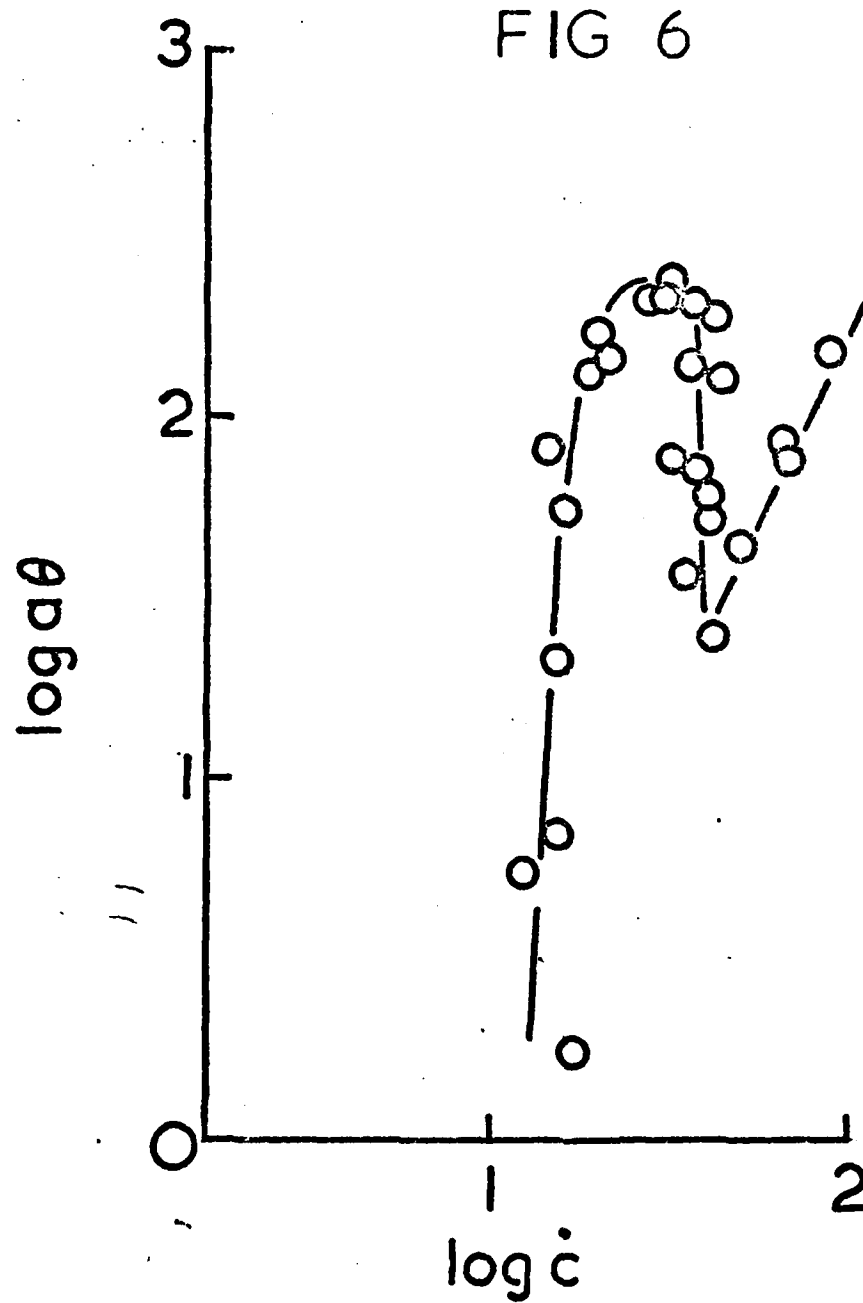


FIG 7

